Structural and Conformational Properties of 2-Propenylphosphine (Allylphosphine) as Studied by Microwave Spectroscopy Supplemented by Quantum Chemical Calculations

Harald Møllendal,*,† Jean Demaison,‡ and Jean-Claude Guillemin§

Department of Chemistry, The University of Oslo, Sem Sælands vei 26, P.O. Box 1033, NO-0315 Oslo, Norway, Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Bât. P5, Université de Lille1, FR-59655 Villeneuve d'Ascq, France, and Laboratoire de Synthèse et Activation de Biomolécules, UMR CNRS 6052, ENSCR, FR-35700 Rennes, France

The microwave spectrum of 2-propenylphosphine (allylphosphine), $H_2C=CH-CH_2-PH_2$, has been investigated in the 7−26.5 and 32−58.5 GHz spectral regions at about −40 °C. Three conformers were assigned. All three rotamers have an anti-clinal ("skew") conformation of the $C=C-C-P$ chain of atoms. The orientation of the phosphino group is different in the three conformers denoted conformer I, II, and III, respectively. A distinction between the three forms can be made with reference to the lone pair (lp) of the phosphino group. In conformer I, the lp−P−C−C link is anti-periplanar, whereas the lp−P−C−C chain is −syn-clinal ("+gauche") in conformer II and +syn-clinal ("−gauche") in conformer III. Conformer I is 1.4(3) kJ/mol more stable than II and 1.6(3) kJ/mol more stable than III. The dipole moment of conformer I was determined to be in units of 10^{-30} C m (note units): $\mu_a = 2.544(14)$, $\mu_b = 0.503(25)$, $\mu_c = 0.438(24)$, and $\mu_{tot} = 2.630(20)$ [$\mu_{tot} = 0.788(6)$ D]. The dipole moment of conformer II is $\mu_a = 1.215(11)$, $\mu_b = 3.14(12)$, $\mu_c = 1.25(49)$, and $\mu_{tot} = 3.59(31)$ [$\mu_{tot} = 1.08(9)$ D], and the dipole moment of conformer III is $\mu_a = 1.567(13)$, $\mu_b = 2.090(21)$, $\mu_c = 1.877(15)$, and $\mu_{tot} = 3.59(31)$ [$\mu_{tot} = 0.964(7)$ D]. Five vibrationally excited states were assigned for conformer I, whereas two excited states were assigned for II as well as one for conformer III. Their vibrational frequencies were determined by relative intensity measurements. Quantum chemical calculations at the B3LYP and MP2 levels of theory reproduced the experimental rotational constants to within a few percent. Much poorer agreement is found for the components of the dipole moments (but the total dipole moment is well reproduced) as well as for the quartic centrifugal distortion constants, the error being mainly systematic in this latter case. The energy differences between the three conformers were calculated both at the Gaussian-2 and at the complete basis set levels of theory with results that are close to the experimental values.

Introduction

Aliphatic phosphines are generally poisonous, pyrophoric, and smell bad. This is assumed to be the reasons that the structural and conformational properties of only a few of them have been investigated in the gaseous state by physical methods such as, for example, microwave (MW) spectroscopy. Studies of $H_2PCH_2CH_3$,[1] $H_2PCH_2CH_2PH_2$,[2] $H_2C=CHPH_2$,[3] $H_2PCH_2CH_2C≡N$,[4] and $H_2PCH_2C≡CH$[5] have shown that phosphines possess unique conformational, structural, and dynamical properties. It was thus felt that it would be of interest if this list were extended to include an allylic phosphine as well. The prototype is 2-propenylphosphine (allylphosphine), $H_2C=CH-CH_2-PH_2$, which was chosen for the present study.

Many studies[6] have shown that allyllic compounds ($H_2C=CH-CH_2-X$) generally prefer to have the $C=C-C-X$ chain of atoms in the anti-clinal (ac) conformation. In some cases, especially for a small X substituent,[6] the syn-periplanar (sp) conformers have been observed. (The obsolete denominations gauche or skew instead of sc, and cis instead of sp are frequently encountered in the literature.)

In $H_2C=CH-CH_2-PH_2$, there is an additional conformational complication caused by the orientation of the phosphino group, which can take three different all-staggered conformations. Five forms that can be distinguished by spectroscopy are then possible. Representatives of these rotamers are depicted in Figure 1.

It is seen in this Figure that there are three $C=C-C-P$ ac rotamers. A distinction between them can be made by reference to the lone electron pair (lp) of the phosphino group. In conformer I (see Figure 1), the $C-C-P-lp$ chain is anti-periplanar (ap). In II, it is −syn-clinal, and in III, it is +syn-clinal. In addition, there are two $C=C-C-P$ sp forms with $C-C-P-lp$ ap (conformer IV) or −sc as in V. Moreover, mirror image conformers exist for all rotamers but IV. The statistical weight of conformer IV is thus 1, whereas the statistical weight of the four other conformers is 2 in each case.

A delicate balance of forces is assumed to dictate the conformational properties of allylphosphine. Three interactions are of special interest: intramolecular hydrogen (H) bonding between the H atoms of the phosphino group and the double bond is the first of these forces. This effect, which must be very weak in this case, is possible in I, III, IV, and V. Internal hydrogen bonding is impossible in conformer II, owing to the orientation of the two H atoms of the phospino group (see Figure 1).

* Corresponding author. E-mail: harald.mollendal@kjemi.uio.no. Tel: +47-22-85-56-74. Fax: +47-22-85-54-41.
† The University of Oslo.
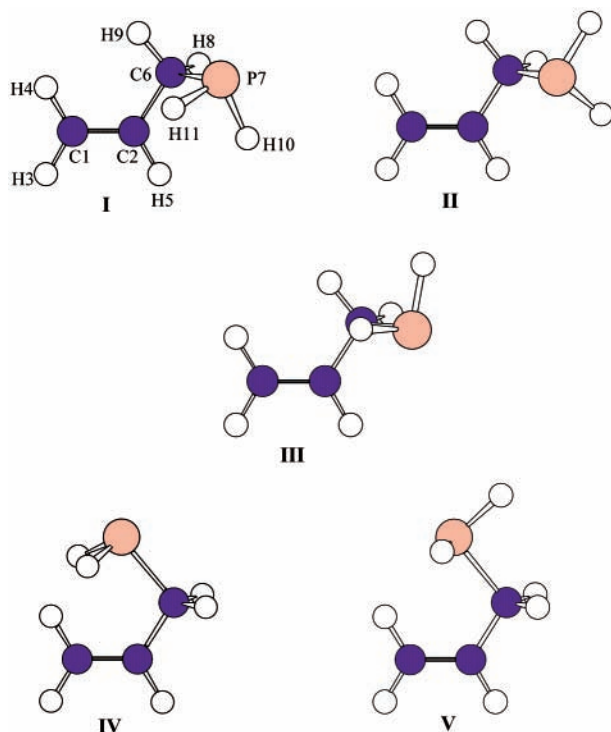‡ Université de Lille1.
§ ENSCR.

Figure 1. Five Possible Conformers of Allylphosphine.

Repulsion between the lone-pair electrons of the phosphino group and the double bond may be another important interaction. This effect should have its minimum in I and IV. Steric repulsion between the rather large phosphino group and the vinyl group may be quite important in conformers IV and V. These and other important questions for this representative of the little-known family of aliphatic phosphines are addressed in the present work.

Experimental Section

Caution: 2-Propenylphosphine is pyrophoric and potentially highly toxic. All reactions and handling should be carried out in a well-ventilated hood.

2-Propenylphosphine has been prepared as previously reported.[7] The reaction of 2-propenyltributylstannane with phosphorus tribromide was followed by the reduction of the formed 2-propenyldibromophosphine with $LiAlH_4$ in tetraglyme. We modified the second step to prepare the 2-propenylphosphine on a gram scale and in pure form: The vacuum line was equipped with two cells with stopcocks. The flask containing the reducing mixture (LAH (1.9 g, 50 mmol)) in tetraglyme (30 mL) was fitted on the vacuum line, cooled to −10 °C, and degassed. The pure 2-propenyldibromophosphine (4.7 g, 20 mmol) was then slowly added with a flex needle through the septum in about 15 min. During and after the addition, the 2-propenylphosphine that formed was distilled off in vacuo from the reaction mixture. A cold trap (−80 °C) selectively removed the less volatile products, and the phosphine was condensed in a second cold trap (−110 °C) to remove the most volatile products (mainly PH_3). After being disconnected from the vacuum line by stopcocks, the product was kept at low temperature (<−40 °C) before analysis. Yield: 1.2 g, 79%. The sample was kept at dry-ice temperature (−80 °C) or in a refrigerator (−40 °C) when not in use.

The MW spectrum was studied using the Oslo Stark spectrometer, which is described briefly in ref 8. A 3 m Stark cell made of brass was utilized. Radio frequency microwave

double resonance (RFMWDR) experiments were carried out as described in ref 9 using the equipment mentioned in ref 10. The 7−26.5 and 32−58.5 GHz spectral regions were investigated with the cell cooled to about −40 °C. Lower temperatures, which would have increased the intensity of the spectrum, could not be employed owing to insufficient vapor pressure of the compound. The pressure was a few Pa when the spectrum was recorded and stored electronically using the program written by Waal.[11] The accuracy of the spectral measurements was better than ±0.10 MHz, and the maximum resolution was about 0.4 MHz.

Results

MW Spectrum and Assignment of the Ground Vibrational State of Conformer I. The quantum chemical calculations (see Table 9, below) predicted that there are rather small energy differences (less than 5 kJ/mol) between all of the five possible rotamers shown in Figure 1. All of these forms are polar, each with a total dipole moment of roughly 3×10^{-30} C m. (Table 10). A rich spectrum was thus expected because several conformers might contribute. The survey spectra indeed confirmed this expectation. Absorption lines were found every few MHz throughout the entire MW range.

The strategy to assign this spectrum was as follows: It is predicted in Table 9 that conformer I is the most stable of the five rotamers. This conformer has its largest dipole moment along the *a* inertial axis. Moreover, this form is rather prolate ($\kappa \approx -0.98$). A relatively strong and simple *a*-type R-branch spectrum was thus predicted to predominate for this rotamer. Such a spectral pattern was indeed found close to the predicted frequencies. The assignments of these transitions were confirmed by Stark effect studies, RFMWDR experiments,[9] and the fit of its transitions to Watson's Hamiltonian.[12]

Searches for *b*-type Q-branch lines were then made. These lines were presumed to be much less intense than the *a*-type transitions already assigned because the μ_b component was predicted to be small (Table 10). Fortunately, these comparatively weak transitions were soon found using a trial-and-error procedure.

The hypothetical frequencies of the ^cQ lines were predicted next. These relatively weak lines were readily found very close to the frequencies predicted for them. Finally, the perpendicular high-*J* P- and R-branch transitions were identified. The rapid Stark effects that these transitions display owing to the K_{-1} near-degeneracy were very helpful. Ultimately, 280 transitions with a maximum *J* value of 76 were assigned.

It was necessary to include all seven Watson sextic centrifugal distortion constants[12] in addition to the quartic ones to get a least-squares fit of the transitions with a root-mean deviation comparable with the experimental uncertainty of ±0.10 MHz. The spectrum is given in the Supporting Information, Table 1S. The resulting spectroscopic constants (*A* reduction, I^r representation[12]) are listed in Table 1.

It is seen that the experimental rotational constants (Table 1) agree to within better than 1% with the ab initio counterparts (Table 10). For the centrifugal distortion constants, the agreement is 1 order of magnitude worse, but the errors are mainly systematic so that the variation of the centrifugal distortion constants may be used to check the assignment.

Vibrationally Excited States of Conformer I. The ^aR transitions of the ground state were accompanied by a weaker but easily discernible series of lines whose Stark and MWRFDR patterns were very similar to those of the ground vibrational state. These transitions were assigned as vibrationally excited

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TABLE 1: Spectroscopic Constants[a,b] of the Ground and the First Excited State of the C1−C2 Torsional Vibration of Conformer I of 2-Propenylphosphine

	ground vibrational state	first excited C−C torsional state
A_v/MHz	18016.4141(53)	18090.811(30)
B_v/MHz	2700.40745(78)	2706.6001(18)
C_v/MHz	2619.24564(76)	2621.0492(18)
Δ_J/kHz	1.82240(84)	1.8660(57)
Δ_{JK}/kHz	−46.039(13)	−46.850(59)
Δ_K/kHz	499.340(49)	490.0(72)
δ_J/kHz	0.225893(38)	0.24559(79)
δ_K/kHz	−18.646(42)	−14.40(41)
Φ_J/Hz	0.00779(19)	0.0^c
Φ_{JK}/Hz	−0.093(12)	−0.95(16)
Φ_{KJ}/Hz	−3.051(49)	0.0^c
Φ_K/Hz	37.42(53)	0.0^c
ϕ_J/Hz	0.003068(13)	0.00192(22)
ϕ_{JK}/Hz	0.853(22)	0.0^c
ϕ_K/Hz	−12.5(23)	0.0^c
no. of transitions[d]	280	94
max J^e	76	46
rms[f]/MHz	0.080	0.095

[a] A reduction, I^r representation.[12] [b] Uncertainties represent one standard deviation. [c] Fixed at this value in the least-squares fit. [d] Number of transitions used in the least-squares fit. [e] Maximum value of the J quantum number. [f] Root-mean-square deviation.

TABLE 2: Spectroscopic Constants[a,b] of Vibrationally Excited States of Conformer I of 2-Propenylphosphine

	second excited C−C torsional state	third excited C−C torsional state
A_v/MHz	18139(19)	18247(23)
B_v/MHz	2712.6864(71)	2718.1781(66)
C_v/MHz	2622.6278(73)	2623.6765(79)
Δ_J/kHz	1.921(29)	1.932(25)
Δ_{JK}^c/kHz	−47.74(12)	−48.64(11)
no of transitions[d]	41	34
max J^e	10	10
rms[f]/MHz	0.118	0.106

	first excited C−P torsional vibration	first excited heavy-atom bending vibration
A_v/MHz	18649(41)	17854(21)
B_v/MHz	2698.1420(61)	2696.5447(68)
C_v/MHz	2616.9789(66)	2615.1050(68)
Δ_J/kHz	1.763(24)	1.763(18)
Δ_{JK}^c/kHz	−45.651(96)	−48.095(56)
no of transitions[d]	43	39
max J^e	10	11
rms[f]/MHz	0.115	0.088

[a] A reduction, I^r representation.[12] [b] Uncertainties represent one standard deviation. [c] Further quartic centrifugal distortion constants fixed at zero in the least-squares fit. [d] Number of transitions used in the least-squares fit. [e] Maximum value of the J quantum number. [f] Root-mean-square deviation.

states of conformer I. It is seen in Tables 2 and 3 that a total of five excited states belonging to three different normal modes have been assigned.

The strongest satellite is assumed to be the first excited state of the torsion around the C2−C6 bond (see Figure 1). A total of 94 transitions with a maximum J value of 46 were assigned for this excited state using the same procedure as used for the ground vibrational state above. The spectroscopic constants are given in Table 1, and the full spectra are listed in Table 2S in the Supporting Information. Two of the sextic centrifugal distortion constants were fitted in this case. The other five sextic constants were preset at zero. Relative intensity measurements

TABLE 3: Stark Coefficients[a] and Dipole Moment[a,b] of Conformer I of 2-Propenylphosphine

		$\Delta\nu E^{-2}/10^{-6}$ MHz V^{-2} cm^2	
transition	$|M|$	obsd	calcd
$2_{0,2} \leftarrow 1_{0,1}$	0	4.61(5)	4.34
	1	3.42(4)	3.45
$2_{1,2} \leftarrow 1_{1,1}$	0	2.57(3)	2.57
$4_{1,4} \leftarrow 3_{1,3}$	1	1.54(2)	1.60
	2	6.64(7)	6.76
	3	15.5(18)	15.4
$4_{1,3} \leftarrow 3_{1,2}$	1	−1.75(2)	−1.70
	2	−6.29(8)	−6.40
	3	−14.0(18)	14.3
$4_{0,4} \leftarrow 3_{0,3}$	1	−1.48(2)	1.48

[a] Uncertainties represent one standard deviation. 1 D = 3.33564 × 10^{-30} C m. [b] Dipole moment/10^{-30} C m. $\mu_a = 2.544(14)$, $\mu_b = 0.503(25)$, $\mu_c = 0.438(24)$, $\mu_{tot} = 2.630(20)$.

performed largely as described in ref 13 yielded 105(20) cm^{-1} for this vibration, compared to 112 cm^{-1} found in the B3LYP calculations (see below).

The a-type R-branch lines of two successively excited states of this mode were assigned next. The b- and c-type spectra were too weak to be assigned in these cases. The spectroscopic constants are found in Table 2. The full spectra are shown in Tables 3S and 4S. Only two of the quartic centrifugal distortion constants (Δ_J and Δ_{JK}) could be fitted in these cases because this conformer is almost a symmetrical top ($\kappa = -0.98$) and because only ^aR lines were assigned. No accurate values of the A rotational constants were obtained (Table 2).

It is seen in Tables 1 and 2 that the B and C rotational constants vary fairly linearly with the excitation of this vibration. This is typical for a harmonic mode.[14]

Two more excited states were identified, as seen in Table 2. The ^aR spectra observed for them are found in the Supporting Information (Tables 5S and 6S). These two excited states are tentatively assigned as the first excited states of the lowest heavy-atom bending vibration and the C−P torsional vibration, respectively. Our reason for these assignments is the magnitude of the changes of the rotational constants. The excitation of the lowest heavy-atom bending mode is expected to lead to comparatively large changes in the rotational constants because relatively large reduced masses are involved in this mode. The opposite is the case for the excitation of the C−P torsion. It is seen in Tables 1 and 2 that the rotational constants of the first excited state of the heavy-atom bending vibration compared to the rotational constants of the ground vibrational state differ much more than in the case of the first excited state of the C−P torsional vibration.

The frequency determined by relative intensity measurements[13] for the first excited state of the heavy-atom bending vibration was 249(40) cm^{-1} compared to 268 cm^{-1} found in the B3LYP calculations below. The frequency of the torsional vibration is likewise 179(30) cm^{-1} compared to 185 cm^{-1} (B3LYP value). There is thus good agreement between the quantum chemical and the experimental values for these three fundamentals.

It should be added that none of the lines observed for this as well as for the two other rotamers assigned in this work was split, owing to the tunneling of the phosphino group. Such splittings have been observed for some of the conformers of other phosphines (e.g., $H_2PCH_2CH_3$,[1] $H_2PCH_2CH_2PH_2$,[2] $H_2C=CHPH_2$,[3] and $H_2PCH_2C\equiv CH$[5]). The tunneling splittings have in these cases[1−3,5] been explained by the existence of mirror images that can be reached by a simple inversion or rotation of

only the phosphino group. This is not possible for the three C≡ C−C−P ac conformers of the title compound. A transformation into a mirror image would in our case involve *both* the phosphino group and a rotation around the C2−C6 bond. The considerably larger reduced masses involved would reduce the tunneling splitting to much less than the resolution of our experiment of about 0.4 MHz.

Dipole Moment of Conformer I. The dipole moment of conformer I was determined in a least-squares fit using the second-order Stark splittings of the ^aR-branch transitions shown in Table 3. The weight of each Stark coefficient was taken to be the inverse square of the standard deviation of that coefficient. The cell was calibrated using OCS, whose dipole moment was taken to be $2.3857(68) \times 10^{-30}$ C m.[15]

The experimental values of the components of the dipole moment along the principal inertial axes $\mu_a = 2.544(14)$, $\mu_b = 0.503(25)$, and $\mu_c = 0.438(24) \times 10^{-30}$ C m agree well with the B3LYP values $\mu_a = 2.41$, $\mu_b = 0.48$, and $\mu_c = 0.68 \times 10^{-30}$ C m (Table 10). The good agreement between the theoretical and experimental dipole moment components provides further evidence that conformer I has indeed been assigned and not confused with II or III, which have similar rotational constants but widely different components of the dipole moment.

Assignment of the Ground Vibrational State of Conformer II. Many comparatively strong transitions remained after the assignments for conformer I had been completed. The quantum chemical calculations indicate that conformer II should be somewhat less stable than I and might thus be present in detectable amounts. It was predicted (Table 10) that μ_b is the largest dipole moment component of this conformer.

Searches were therefore first made for the b-type Q-branch transitions among the strongest unassigned lines using a trial-and-error procedure. These searches soon met with success. Attempts to assign the ^cQ transitions, which are the strongest ones of the c-type lines, were made next. These trials failed, even though the frequencies of the ^cQ transitions can be predicted accurately from those of the ^bQ transitions. The reason for this failure is assumed to be the small μ_c component (see the next paragraph) producing insufficient intensities.

Attention was then focused on finding the ^bR-branch transitions. A trial-and-error procedure was again successful after many trials. It was ultimately possible to include P- and R-branch transitions with rather high values of the quantum number J (up to $J = 74$). Finally, the comparatively weak ^aR-branch transitions were assigned. The full spectrum is given in Table 7S in the Supporting Information. The spectroscopic constants obtained from 322 transitions are listed in Table 4. There is again very good agreement between the experimental (Table 4) and theoretical rotational constants and quartic centrifugal distortion constants (Table 10).

Vibrationally Excited States of Conformer II. Two vibrationally excited states of this rotamer were assigned. It was possible to find only the ^bQ transitions in these cases. It was therefore not possible to determine all three rotational constants. Only $A - C$ and the asymmetry parameter $\kappa = (2B - A - C)/(A - C)$ could be found together with four of the quartic and three of the sextic centrifugal distortion constants in the case of the first excited state and one sextic constant for the second excited state; see Table 5. The spectra are found in Tables 8S and 9S, respectively.

Relative intensity measurements yielded 88(30) cm^{-1} for the frequency of the first excited state, in reasonable agreement with 95 cm^{-1} obtained in the B3LYP calculations.

TABLE 4: Spectroscopic Constants^{a,b} of the Ground Vibrational State of Conformer II of 2-Propenylphosphine

	ground vibrational state
A_v/MHz	17193.8004(55)
B_v/MHz	2785.36567(86)
C_v/MHz	2680.43983(94)
Δ_J/kHz	3.0034(15)
Δ_{JK}/kHz	−70.484(25)
Δ_K/kHz	638.419(62)
δ_J/kHz	0.49092(32)
δ_K/kHz	−14.974(76)
Φ_J/Hz	0.02291(88)
Φ_{JK}/Hz	−0.161(29)
Φ_{KJ}/Hz	−2.85(12)
Φ_K/Hz	50.39(86)
ϕ_J/Hz	0.00974(20)
ϕ_{JK}/Hz	−3.083(35)
ϕ_K/Hz	23.87(79)
no. of transitions^c	322
max J^d	74
rms^e/MHz	0.097

^{a} A reduction, I^r representation.[12] ^{b} Uncertainties represent one standard deviation. ^{c} Number of transitions used in the least-squares fit. ^{d} Maximum value of the J quantum number. ^{e} Root-mean-square deviation.

TABLE 5: Spectroscopic Constants^{a,b} of the First and Second Excited States of the C−C Torsional Vibration of Conformer II of 2-Propenylphosphine

	first excited C−C torsional state	second excited C−C torsional state
$(A_v - C_v)$/MHz	14496.603(56)	14496.595(56)
κ	−0.984204	−0.982899
Δ_J/kHz	3.0034^c	3.0034^c
Δ_{JK}/kHz	−71.894(81)	−70.42(14)
Δ_K/kHz	567(13)	638.61^c
δ_J/kHz	0.57753(28)	0.6049(10)
δ_K/kHz	−7.623(64)	−10.71(27)
Φ_{JK}/Hz	0.801(49)	0.0^c
Φ_{KJ}/Hz	−152(13)	0.0^c
ϕ_J^g/Hz	0.01545(12)	0.00415(84)
no. of transitions^d	63	29
max J^e	49	35
rms^f/MHz	0.110	0.110

^{a} A reduction, I^r representation.[12] ^{b} Uncertainties represent one standard deviation. ^{c} Fixed at this value in the least-squares fit. ^{d} Number of transitions used in the least-squares fit. ^{e} Maximum value of the J quantum number. ^{f} Root-mean-square deviation. ^{g} Further sextic constants preset at zero.

Dipole Moment of Conformer II. The dipole moment of conformer II was determined in the same way as the dipole moment of conformer I. The results are shown in Table 6. Accurate values were determined for μ_a and μ_b, whereas μ_c comes with a much larger standard deviation. There is fairly good agreement between the theoretical B3LYP dipole moment components for conformer II (Table 10) and those shown in Table 6. It is thus unlikely that conformer II has been confused with III.

Assignment of the Ground Vibrational State of Conformer III. Many relatively strong lines remained unassigned even after several hundred transitions had been identified for conformers I and II. μ_b was also predicted to be the largest dipole moment component for this rotamer (Table 10). Attempts were first made to assign the ^bQ-branch transitions of conformer III by employing a trial-an- error procedure. These attempts were successful after intensive searching. The weaker ^cQ-branch lines were assigned next. Searches were then made for the ^bR-branch transitions, which were identified after much searching. ^aR- and

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TABLE 6: Stark Coefficients[a] and Dipole Moment[a,b] of Conformer II of 2-Propenylphosphine

transition	$|M|$	$\Delta\nu\,E^{-2}/10^{-5}$ MHz V^{-2} cm^2	
		obsd	calcd
$3_{1,2} \leftarrow 3_{0,0}$	3	1.47(3)	1.47
$4_{1,3} \leftarrow 4_{0,4}$	4	1.27(3)	1.31
$5_{1,4} \leftarrow 5_{0,5}$	5	1.25(3)	1.25
$6_{1,5} \leftarrow 6_{0,6}$	6	1.16(3)	1.21
	5	0.815(7)	0.779
$7_{2,5} \leftarrow 7_{1,6}$	7	2.54(5)	2.63
	6	2.18(3)	2.13
$8_{1,7} \leftarrow 8_{0,8}$	8	1.13(2)	1.14
	7	1.00(8)	0.97

[a] Uncertainties represent one standard deviation. 1 D = 3.33564 × 10^{-30} C m. [b] Dipole moment/10^{-30} C m. $\mu_a = 1.215(11)$, $\mu_b = 3.14(12)$, $\mu_c = 1.25(49)$, $\mu_{tot} = 3.59(31)$.

TABLE 7: Spectroscopic Constants[a,b] of the Ground and First Excited State of the C−C Torsional Vibration of Conformer III of 2-Propenylphosphine

	ground vibrational state	first excited C−C torsional state
A_v/MHz	17707.3814(38)	17724.4606(51)
B_v/MHz	2758.26622(58)	2772.65568(73)
C_v/MHz	2655.97078(57)	2663.26559(70)
Δ_J/kHz	2.55101(75)	2.65621(95)
Δ_{JK}/kHz	−63.841(12)	−64.225(16)
Δ_K/kHz	614.782(37)	613.956(49)
δ_J/kHz	0.370129(48)	0.420783(76)
δ_K/kHz	−16.719(40)	−12.553(67)
Φ_J/Hz	0.01344(22)	0.01671(30)
Φ_{JK}/Hz	−0.5870(94)	−0.424(17)
Φ_{KJ}/Hz	−2.222(30)	−2.310(39)
Φ_K/Hz	45.59(25)	43.03(39)
ϕ_J/Hz	0.006616(29)	0.007295(53)
ϕ_{JK}/Hz	0.725(29)	1.139(58)
ϕ_K/Hz	−35.22(70)	−13.3(20)
no. of transitions[c]	481	385
max J^d	74	63
rms[e]/MHz	0.079	0.085

[a] A reduction, I^r representation.[12] [b] Uncertainties represent one standard deviation. [c] Further quartic centrifugal distortion constants fixed at zero in the least-squares fit. [d] Number of transitions used in the least-squares fit. [e] Maximum value of the J quantum number.

[c]R-branch transitions were then assigned with ease. These assignments were gradually extended to high values of J ($J = 74$). The 481 transitions given in Table 10S in the Supporting Information were used to derive the spectroscopic constants listed in Table 7. Accurate values were derived even for the sextic centrifugal distortion constants in this case.

Vibrationally Excited State of Conformer III. One vibrationally excited state of this rotamer was assigned. The spectrum (385 transitions) is found in Table 11S. The spectroscopic constants are given in Table 7. Relative intensity measurements yielded 95(25) cm^{-1} for this vibration that is assumed to be the first excited state of the C−C torsional vibration. The B3LYP frequency was 99 cm^{-1}.

Dipole Moment of Conformer III. The dipole moment of conformer III was determined in the same manner as described above. The results are given in Table 8. There is again reasonably good agreement between the B3LYP predictions for the dipole moment components and the values given in the last mentioned table. The same can be said for the rotational constants.

Searches for Conformers IV and V. The assignments reported above include about 1800 transitions that were used to derive the spectroscopic constants. Many additional lines were

TABLE 8: Stark Coefficients[a] and Dipole Moment[a,b] of Conformer III of 2-Propenylphosphine

transition	$|M|$	$\Delta\nu\,E^{-2}/10^{-6}$ MHz V^{-2} cm^2	
		obsd	calcd
$4_{1,3} \leftarrow 4_{0,4}$	4	8.42(10)	8.65
	3	3.68(5)	3.66
$5_{1,4} \leftarrow 5_{0,5}$	5	7.61(8)	7.70
	4	4.44(5)	4.31
$6_{1,5} \leftarrow 6_{0,6}$	6	6.23(5)	6.31
$7_{1,6} \leftarrow 7_{0,7}$	7	6.81(8)	6.80
$3_{1,2} \leftarrow 3_{0,3}$	3	11.70(13)	11.67
$2_{1,2} \leftarrow 2_{0,2}$	2	−18.00(20)	17.99
$7_{1,7} \leftarrow 7_{0,7}$	7	6.90(8)	6.80
	6	4.61(5)	4.61

[a] Uncertainties represent one standard deviation. 1 D = 3.33564 × 10^{-30} C m. [b] Dipole moment/10^{-30} C m. $\mu_a = 1.567(13)$, $\mu_b = 2.090(21)$, $\mu_c = 1.877(15)$, $\mu_{tot} = 3.217(22)$.

assigned but not included in the fits because they were not well resolved from overlapping transitions. However, the strongest lines seen in the spectrum have all been assigned to one of the three rotamers. The same is the case for the majority of the lines of intermediate intensity. It should be remarked that a large number of weak transitions were not assigned. Many of these lines, perhaps most, undoubtedly belong to unassigned vibrationally excited states of the three rotamers assigned above. Impurities cannot of course be ruled out in this case.

Extensive searches including the use of the powerful and sensitive RFMWDR technique were finally made in a futile attempt to find conformers IV and V. Intensity considerations of unassigned transitions coupled with the dipole moments predicted for these two hypothetical forms lead us to conclude that each of them is at least 3 kJ/mol less stable than conformer I. This estimate is considered to be conservative and in agreement with the theoretical predictions in Table 10.

Energy Differences between the Conformers. The internal energy differences between the ground vibrational states of conformers I, II, and III were determined by comparing the intensities of selected low-J transitions of the ground state of the three forms assuming a Boltzmann distribution. The three rotamers were assumed to have the same statistical weight. The experimental dipole moments reported above were used. The precautions of ref 13 were observed. Conformer I was found to be the most stable one of the three. This rotamer is 1.4(3) kJ/mol more stable than II and 1.6(3) kJ/mol more stable than III. These energy differences agree well with the G2 and CBS calculations shown in Table 9.

Quantum Chemical Calculations. Before starting the analysis of a microwave spectrum as dense as this one of 2-propenylphosphine, it is useful to perform ab initio calculations that supply approximate values of parameters that make the assignment much easier: the energy difference between the conformers, rotational and quartic centrifugal distortion constants, components of the electric dipole moment, and frequencies of the lowest vibrational modes. All of the calculations were performed with the Gaussian-94 program package.[17]

First, the energy differences between the conformers (see Figure 1) were calculated in order to determine which forms are the most stable. To attempt to obtain reliable results, two compound methods have been used: the Gaussian-2 (G2) theory[18] and the complete basis set (CBS-Q) method.[19] Both methods are known to give accurate energies and were used as implemented in the Gaussian-94 program. The G2 calculations were repeated for the structurally similar compound 2-propenylamine, $H_2NCH_2CH\text{=}CH_2$, because we think it is of interest

TABLE 9: Selected Structural Parameters of 2-Propenylphosphine and Energy Differences (in kJ/mol) between Conformers of 2-Propenylphosphine and 2-Propenylamine[a]

	I	II	III	IV	V
∠(C=C−C−P)	anti-clinal	anti-clinal	anti-clinal	syn-periplanar	syn-periplanar
∠(lp-P−C−C)	anti-periplanar	−syn-clinal	+syn-clinal	anti-periplanar	−syn-clinal
P/LEP[b]	gauche/trans	gauche/gauche1	gauche/gauche2	cis/trans	cis/gauche
∠(C=C−C−P)	113.8	106.5	115.3	0.0	−5.8
∠(H$_1$−P−C−C)	48.8	159.3	−173.1	47.4	170.9
∠(H$_2$−P−C−C)	−45.5	65.3	−78.5	−47.4	76.7
∠(C=C−C)	125.2	125.3	124.9	128.0	127.2
∠(C−C−P)	117.7	111.1	110.8	121.5	115.6
ΔE(G2)	0.00	2.13	1.34	3.27	4.31
ΔE(CBS-Q)	0.00	2.66	1.73	3.91	4.56
ΔE(exp)	0.00	1.4(3)	1.6(3)		
2-propenylamine					
ΔE(G2)	0.62	6.60	0.28	0.00	2.01

[a] The angles (in degrees) are calculated at the B3LYP/6-311++G(3df,2pd) level of theory. See text for the notations. [b] Notation of ref 16.

TABLE 10: Calculated Rotational Constants, Dipole Moments, and Centrifugal Distortion Constants of 2-Propenylphosphine[a]

	I anti-clinal anti-periplanar calcd	e. -c. (%)	II anti-clinal −syn-clinal calcd	e. -c. (%)	III anti-clinal +syn-clinal calcd	e. -c. (%)	IV syn-periplanar anti-periplanar calcd	V syn-periplanar −syn-clinal calcd
C=C−C−P lp-P−C−C								
				MP2(ae)/6-31G*				
A	17 854	0.9	17 024	1.0	17 276	2.4	12 638	12 432
B	2703	−0.1	2796	−0.4	2789	−1.1	3434	3581
C	2622	−0.1	2690	−0.4	2678	−0.8	2812	2887
				B3LYP/6-311++G(3df,2pd)				
A	18 163.4	−0.8	17 332.2	−0.8	18 017.7	−1.8	12 866.9	12 614.1
B	2674.99	0.9	2751.16	1.2	2715.7	1.5	3375.6	3521.35
C	2596.77	0.9	2651.15	1.1	2621.44	1.3	2781.76	2857.5
μ_a	2.41	−5.7	1.03	−18.2	−1.47	6.6	3.17	1.15
μ_b	0.48	−5.1	3.02	−3.9	2.28	8.5	1.35	3.66
μ_c	0.91	52.0	1.70	26.3	1.99	5.7	0.00	1.70
μ_t	2.62	−0.5	3.61	0.6	3.37	4.5	3.45	4.20
Δ_J	1.52	17	2.32	23	2.04	20		
Δ_{JK}	−36.86	20	−53.03	25	−49.70	22		
Δ_K	412.9	17	492.2	23	524.7	15		
δ_J	0.1827	19	0.3654	26	0.2736	26		
δ_K	−13.11	30	−5.44	64	−16.04	4		

[a] Rotational constants in MHz, dipole moments in 10^{-30} C m, and centrifugal distortion constants in kHz.

to compare the properties of amines and phosphines. The results are given in Table 9.

The rotational constants and dipole moment components were calculated using density functional theory with the hybrid functional B3LYP (Becke's three-parameter functional employing the Lee, Yang, and Parr correlation functional).[20] This method was often shown to be in good agreement with experiment.[21] The 6-311++G(3df,2pd) basis set was used. To check the reliability of the calculated parameters, second-order Møller−Plesset perturbation theory (MP2)[22] was also used with the 6-31G* basis set, all electrons being correlated. This latter method was found to give slightly more accurate rotational constants than the B3LYP calculations in the cases of 2-propynylphosphine[5] and vinylphosphine.[3] The harmonic force field and the quartic centrifugal distortion constants were calculated at the B3LYP/6-311++G(3df,2pd) level of theory. The results are given in Table 10. The full MP2 as well as B3LYP structures of the conformers are found in the Supporting Information, Table 12S. Moreover, MP2 calculations of the structures of the corresponding conformers of H$_2$NCH$_2$CH=CH$_2$ are reported in the Supporting Information, Table 13S.

Discussion

Several interesting observations are made in the present work. The MP2 calculations (Table 12S) predict longer CC and CH bond lengths and shorter CP and PH bond lengths than the B3LYP method does. Both procedures give angles that are in good agreement, except for some dihedral angles where a difference up to 4° may be found. This difference is mainly due to the 6-31G* basis set, which seems to be too small in this case. MP2 calculations for one rotamer using the 6-311++G-(3df,2pd) basis set gave results in excellent agreement with the B3LYP values, but these new MP2 calculations take almost two 2 days compared to a few minutes using the 6-31G* basis set. Calculations at this level of theory were therefore not made for all five conformers.

The deviation between the observed and calculated values of the A rotational constants is better than 2.4% (Table 12S). The B and C rotational constants are predicted to be within better than 1.5% of the experimental values in both the MP2 and B3LYP calculations.

The theoretical quartic centrifugal distortion constants (Table 12S) are in rather poor agreement with the experimental values (up to 26%, δ_K values being excluded), but as the error is mainly systematic, scaling should improve the theoretical force field considerably.

The B3LYP values for the total dipole moments (Table 12S) are in good agreement with the corresponding experimental values, but the agreement is much poorer for some components. This may be due to the inaccuracy of the theoretical structure.

An ab initio calculation using the very large quadruple-ζ cc-pV(Q+d)Z basis set of Dunning et al.[23] at the B3LYP level gives a structure and a dipole moment almost identical to the 6-311++G(3df,2pd) values. Thus, to improve the accuracy of the calculations, it would be necessary to use a method more expensive than either the MP2 or B3LYP procedures.

It is seen in Table 9 that both II and III are found to be about 1.5 kJ/mol less stable than I. The G2 and CBS-Q predictions lie within about 1 kJ/mol of this value, which is quite satisfactory. Moreover, it is noted that conformer III is calculated to be slightly more stable than II in the G2 as well as in the CBS-Q method, whereas the opposite is found experimentally (Table 9). The reason that both calculations predict this energy difference in the wrong direction is unknown. The fact that conformers IV and V are predicted to be considerably less stable than I, II, and III is in agreement with the MW observations.

There are probably several reasons that conformer I is the most stable form: The lone electron pair points away from the double bond, thus minimizing the repulsive interaction between the two electron clouds. A weak internal H bond formed between H_{11} and the π electrons may exist, as indicated by the rather short $H_{11} \cdots C_2$ distance (about 290 pm). This interaction would stabilize I. The lone electron pair has a less favorable orientation in II and III, which may partly explain why they are less stable than I.

It is noted in Table 9 that the C=C−C angle is 2−3° larger in conformers IV and V than in the three other forms. This may reflect a repulsion caused by the large size of the phosphino group. It is possible that this interaction is the main explanation why IV and V are less stable than the three other rotamers.

Interestingly, the conformational makeup of 2-propenylphosphine is strikingly different from that of its amino congener, $H_2NCH_2CH=CH_2$, where four rotamers have been found by MW spectroscopy.[16] The quantum chemical calculations (Tables 9 and 13S) for the amine indicate that conformers similar to I, III, and IV have about the same energy, whereas those similar to II and V are predicted to be approximately 6 and 2 kJ/mol, respectively, less stable. The explanation of the conformational difference between the amine and the title compound is obviously quite complex. The fact that the amine will form stronger H bonds than the phosphine, the lone electron pair of the N atom is smaller and less diffuse than that of the P atom, and the amino group is smaller than the phosphino group are factors that are important for the observed conformational difference.

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